

NO DRAWINGS

- (21) Application No. 47924/70 (22) Filed 8 Oct. 1970
 (31) Conventional Application No. 80540 (32) Filed 8 Oct. 1969 in
 (33) Japan (JA)
 (45) Complete Specification published 23 Aug. 1972
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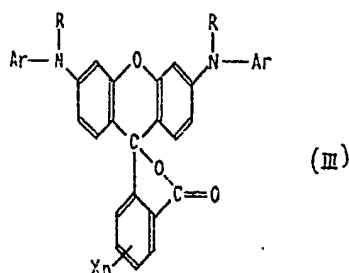


(54) PROCESS FOR PREPARING FLUORANE COMPOUNDS

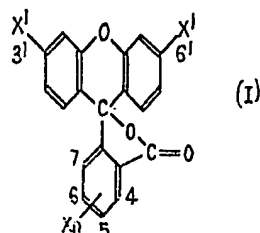
(71) We, FUJI PHOTO FILM CO., LTD.,
 a Japanese Company, of No. 210, Nakanuma,
 Minami Ashigara-Machi, Ashigara-Kamigun,
 Kanagawa, Japan, do hereby declare the
 invention for which we pray that a patent
 may be granted to us, and the method by
 which it is to be performed, to be particu-
 larly described in and by the following state-
 ment:—

The present invention relates to a process
 for preparing fluorane compounds.

According to the invention, there is pro-
 vided a process for preparing a fluorane com-
 pound represented by the general formula
 (III):



wherein X represents a halogen atom, n is
 an integer from 1 to 4, R represents an alkyl
 group having from 1 to 5 carbon atoms and
 Ar represents an aryl group, which comprises
 condensing a fluorane derivative represented
 by the general formula (I):



wherein X' represents a halogen atom and X
 and n are as defined above with an arylamine
 derivative represented by the general formula
 (II):



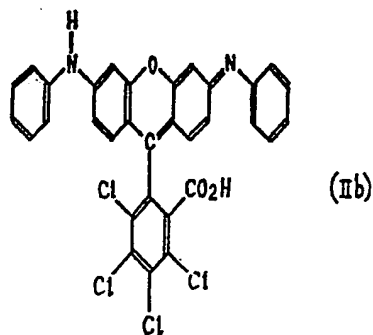
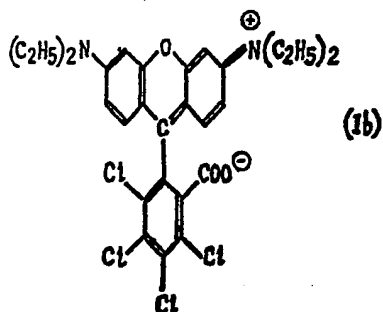
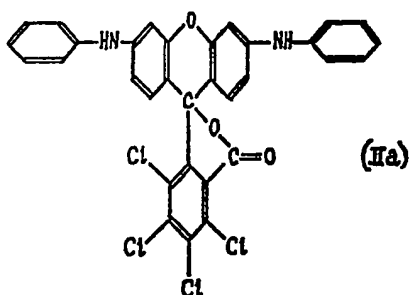
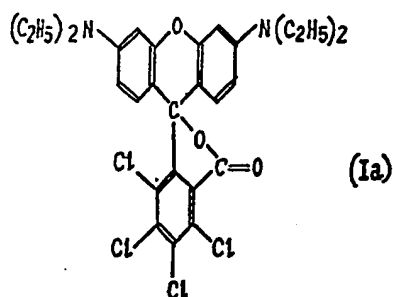
wherein R and Ar are as defined above and
 R' represents a hydrogen atom or a methyl,
 ethyl, benzyl, allyl or acetyl group.

The fluorane compounds represented by the
 general formula (III) as claimed in our co-
 pending U.K. application No. 47923/70
 (Serial No. 1273454), wherein an alternative
 process for preparing them is also claimed.
 These compounds are substantially colourless
 in themselves but when contacted with solid
 acids such as bentonite, zeolite, acid clay or
 trimagnesium silicate, organic acids such as
 benzoic acid, benzenesulphonic acid or phenol,
 or mineral acids such as hydrochloric acid,
 sulphuric acid or perchloric acid, that is, so-
 called electron acceptor materials, the fluorane
 compound is immediately converted into a
 dye having a colour varying from purple to
 blue according to the particular fluorane com-
 pound.

The fluorane compounds represented by
 the general formula (III) are very stable on
 exposure to the atmosphere or light and their
 colour-forming ability is not affected by such
 exposure. Also, the dye formed on contact
 with an electron-acceptor material is very
 fast to light. The fluorane compounds repre-
 sented by the general formula (III), there-
 fore, are very effective as precursors or colour-
 formers for pressure-sensitive, heat-sensitive
 and photo-sensitive copying papers (these are
 developed by contact with an electron
 acceptor material under pressure, heat or
 light).

Several compounds similar to those repre-
 sented by the general formula (III) are known
 (see Beilstein, Handbuch Der Organische
 Chemie, Vol. 19, 349). Examples of these
 known compounds are represented by the
 following formulae Ia and IIa but these com-
 pounds cannot be obtained as colourless
 crystals. It is believed that they exist rather
 in the forms represented by the following
 formulae Ib and IIb, which are dyes:

SEE ERRATA SLIP ATTACHED



5 The inventors have found that replacement of the dialkylamino and monoarylamino groups with N - alkyl - N - arylamino groups renders the lactone ring stable, so that the desired compound is obtained as a colourless material.

10 The compounds represented by the general formula (I) may be selected from hitherto

known compounds such as 3',4',4,5,6,7, - hexachlorofluorane and 3',6',4,7 - tetrachlorofluorane.

3',6' - Dichloro - 4,5,6,7 - tetrabromo - fluorane and 3',6' - dibromo - 5 - iodo - fluorane can be obtained by chlorinating or brominating the hydroxy groups of the corresponding fluorescein (3',6' - dihydroxy - fluorane) with phosphorus pentachloride or phosphorus pentabromide.

The compounds of the general formula (II) include N - methylaniline, N,N - dimethylaniline, N - allyl - N - methylaniline, N - methyl acetanilide, N - ethylaniline, N,N - diethylaniline, N - benzyl - N - ethylaniline, N - methyl - o - toluidine, N - methyl - o - anisidine, N - ethyl - p - anisidine, N - methyl - p - chloroaniline, N,N - dimethyl - p - chloroaniline, N - methyl - m - chloroaniline and N - methyl - β - naphthylamine.

The condensation reaction between the fluorane derivative represented by the general formula (I) and the arylamine derivative represented by the general formula (II) can be carried out by heating these compounds in the presence of zinc chloride and/or p - toluenesulphonic acid. The reaction may be conducted at 60—230°C, preferably 170—200°C, for from 1 to 6 hours.

The fluorane derivatives prepared by the process of the invention may be employed as precursor pigments in pressure, heat or light-sensitive copying papers.

The process of the invention is highly suitable for industrial use.

The following examples illustrate the present invention.

EXAMPLE 1

Preparation of 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane.

A mixture of 10.2 g. (0.02 mole) of 3',6', 4,5,6,7 - hexachloro - fluorane, 6.4 g. (0.06 mole) of N - methylaniline and 10 g. of zinc chloride was heated for 2 hours at 180—185°C., for 2 hours at 190—195°C. and for 2 hours at 210—220°C. The dye formed in the reaction was then dissolved in methanol, and poured into a large quantity of water. The precipitated dye was filtered off under suction, and washed with a small quantity of dilute hydrochloric acid.

On violently stirring the dye in a suspension of 300 ml. of 3% aqueous caustic soda solution and 300 ml. of toluene, the product formed by neutralization of said dye dissolved in the toluene.

The toluene layer was separated, washed several times with warm water and concentrated by evaporation under reduced pressure. The syrup-like matter obtained was mixed with a small quantity of acetone and cooled to obtain 4.2 g. of 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachloro -

fluorane as faint greyish-blue crystals melting at 240—241°C.

- 5 A toluene solution of the compound was completely colourless but developed a slightly purplish blue colour immediately on contact with electron acceptor materials such as acid clay, benzenesulphonic acid and hydrochloric acid.

EXAMPLE 2

- 10 Example 1 was repeated three times but using 7.3 g. (0.06 mole) of N,N - dimethylaniline, 8.8 g. (0.06 mole) of N - allyl - N - methylaniline or 8.9 g. (0.06 mole) of N - methylacetanilide instead of the 6.4 g. (0.06 mole) of N - methylaniline to obtain in each case the same compound as in Example 1, in nearly the same yield (30—35%).

EXAMPLE 3

- 20 Preparation of 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane.

- 25 A mixture of 10.2 g. (0.02 mole) of 3',6', 4,5,6,7 - hexachloro - fluorane, 7.3 g. (0.06 mole) of N - ethylaniline, 15 g. of zinc chloride and 5 g. of *p* - toluenesulphonic acid was reacted for 2 hours at 180—185°C., for 2 hours at 200—210°C and for 1 hour at 220—230°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 4.8 g of 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane as faint greyish-blue crystals melting at 225°C.

- 35 This compound developed a slightly purplish blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 4

- 40 Example 3 was repeated twice but using 8.9 g. (0.06 mole) of N,N - diethylaniline or 7.3 g. (0.06 mole) of N - ethylaniline. In each case, the same compound as in Example 3, i.e., 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane was obtained in nearly the same yield (35—37%).

EXAMPLE 5

- 45 Preparation of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

- 50 Example 1 was repeated except that 7.3 g. (0.06 mole) of N - methyl - *o* - toluidine was used instead of 6.4 g. (0.06 mole) of N - methyl aniline to obtain 4.5 g. of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 4,5,6,7 - tetrachlorofluorane as faint purplish crystals melting at 259—261°C.

- 55 This fluorane compound developed a purple colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 6

- 60 Preparation of 3',6' - bis[N - methyl -

N - (*o* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

Example 1 was repeated except that 8.2 g. (0.06 mole) of N - ethyl - *o* - anisidine was used instead of 6.4 g. (0.06 mole) of N - methylaniline to obtain 5.4 g. of 3',6' - bis[N - methyl - N - (*o* - anisyl)amino] - 4,5,6,7 - tetrachlorofluorane as faint purple crystals melting at 213°C.

Said fluorane compound developed a purplish-blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 7

Preparation of 3',6' - bis[N - ethyl - N - (*p* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

Example 1 was repeated except that 9.1 g. (0.06 mole) of N - ethyl - *p* - anisidine was used instead of 6.4 g. (0.06 mole) of N - methylaniline to obtain 5.7 g. of 3',6' - bis[N - ethyl - N - (*p* - anisyl)amino] - 4,5,6,7 - tetrachlorofluorane as faint greyish-blue crystals melting at 231—232°C.

This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 8

Preparation of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

Example 3 was repeated except that 8.5 g. (0.06 mole) of N - methyl - *p* - chloroaniline was used instead of 7.3 g. (0.06 mole) of N - ethylaniline to obtain 4.4 g. of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 223°C. This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 9

Preparation of 3',6' - bis[N - methyl - N - (*m* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

Example 3 was repeated except that 8.5 g. (0.06 mole) of N - ethyl - (*m* - chloroaniline) was used instead of 7.3 g. (0.06 mole) of N - ethylaniline to obtain 4.2 g. of 3',6' - bis[N - methyl - N - (*m* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 160—162°C.

This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 10

Preparation of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] 4,5,6,7 - tetrabromo - fluorane.

A mixture of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane, 9.3

- g. (0.06 mole) of N,N - dimethyl *p* - chloro-aniline, 10 g. of zinc chloride and 5 g. of *p* - toluenesulphonic acid was reacted for 2 hours at 185—195°C., for 2 hours at 205—210°C. and for 1 hour at 220—230°C. to obtain 6.3 g. of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrabromo - fluorane as colourless crystals melting at 248—250°C.
- 10 This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 11

- 15 Preparation of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,7 - dichloro - fluorane.

- Example 10 was repeated except that 8.8 g. (0.02 mole) of 3',6',4,7 - tetrachloro - fluorane was used instead of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane to obtain 3.2 g. of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,7 - dichloro - fluorane.

- 20 Example 10 was repeated except that 8.8 g. (0.02 mole) of 3',6',4,7 - tetrachloro - fluorane was used instead of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane to obtain 3.2 g. of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,7 - dichloro - fluorane as colourless crystals melting at 200—202°C.

- 30 This compound developed a slightly purplish blue colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 12

- 35 Preparation of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 5 - iodo - fluorane.

- 40 A mixture of 11.7 g. (0.02 mole) of 3',6' - dibromo - 5 - iodo - fluorane, 7.3 g. (0.06 mole) of N - methyl - *o* - toluidine and 10 g. of zinc chloride was reacted for 2 hours at 185—190°C. and for 2 hours at 200—205°C. to obtain 5.8 g. of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 5 - iodo - fluorane as faint purple crystals melting at 195—198°C.
- 45 This compound developed a purple colour on contact with an electron acceptor material as in Example 1.

EXAMPLE 13

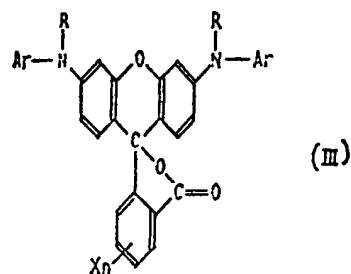
- 50 Preparation of 3',6' - bis[N - methyl - N - (*β* - naphthyl)amino] - 4,5,6,7 - tetrachloro - fluorane.

- 55 Example 3 was repeated except that 9.4 g. (0.06 mole) of N - methyl - *β* - naphthylamine was used instead of 7.3 g. (0.06 mole) of N - ethylaniline to obtain 2.4 g. of 3',6' - bis[N - methyl - N - (*β* - naphthyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 274—276°C.

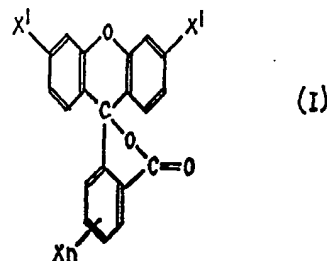
This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

WHAT WE CLAIM IS:—

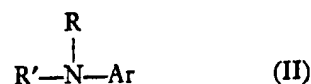
1. A process for preparing a fluorane compound represented by the general formula (III):



wherein X represents a halogen atom, n is an integer from 1 to 4, R represents an alkyl group having from 1 to 5 carbon atoms and Ar represents an aryl group, which comprises condensing a fluorane derivative represented by the general formula (I):



wherein X' represents a halogen atom and X and n are as defined above with an arylamine derivative represented by the general formula (II):



wherein R and Ar are as defined above and R' represents a hydrogen atom or a methyl, ethyl, benzyl, allyl or acetyl group.

2. A process as claimed in Claim 1, wherein the condensation is conducted in the presence of zinc chloride and/or *p* - toluenesulphonic acid.

3. A process as claimed in Claim 1 or 2, wherein the condensation is conducted at a temperature from 60 to 230°C for from 1 to 6 hours.

4. A process as claimed in claim 3, wherein the condensation is conducted at a temperature from 170°C. to 200°C.

5. A process for preparing a fluorane compound as claimed in claim 1, substantially as hereinbefore described with reference to any of the Examples.

GEE & CO.,
Chartered Patent Agents,
51/52, Chancery Lane,
London, W.C.2.
Agents for the Applicants.

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PATENT SPECIFICATION

(11) 128

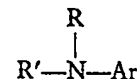
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wherein R and Ar are as defined above
 R' represents a hydrogen atom or a

ERRATA

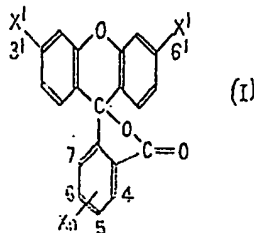
SPECIFICATION No. 1,286,885

Page 4, line 6 for 3',6 read 3',6'

Page 4, lines 17 to 23, Delete whole lines

THE PATENT OFFICE
 16th October 1972

wherein X represents a halogen atom; n is
 an integer from 1 to 4, R represents an alkyl
 group having from 1 to 5 carbon atoms and
 Ar represents an aryl group, which comprises
 condensing a fluorane derivative represented
 by the general formula (I):



wherein X' represents a halogen atom and X
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